Effects of disorder on the optical properties of the (Zn,Mg)(S,Se) quaternary alloy

Antonino Marco Saitta,[1,a] Stefano de Gironcoli,[1,b] and Stefano Baroni[1,2,c]

[1] *INFM – Istituto Nazionale per la Fisica della Materia and*

SISSA – Scuola Internazionale Superiore di Studi Avanzati, Via Beirut 2-4, I-34014 Trieste, Italy

[2] *CECAM – Centre Européen de Calcul Atomique et Moléculaire, ENSL, 46 Allée d'Italie, 69364 Lyon Cedex 07, France*

(February 1, 2008)

The electronic and optical properties of (Zn,Mg)(S,Se) wide-gap solid solutions are studied using *ab initio* techniques and starting from the previously determined atomistic structure of the alloy. Compositional disorder is shown to close substantially the gap with respect to the predictions of the virtual-crystal approximation. The bowing of the fundamental gap vs. composition predicted by our calculations is in very good agreement with experiments available for the Zn(S,Se) pseudo-binary alloy. At temperatures typical for MBE growth, the quaternary alloy displays a rather large amount of short-range order whose effect is to slightly but unmistakably open the gap. Our results agree well with recent experimental data for the quaternary alloy.

In the last decade much effort has been devoted to the study of semiconducting materials capable of operating in the short wavelength optical range. The main goal of these efforts is the realization of light-emitting and laser diodes encompassing the entire visible-light window and, in perspective, the industrial-scale production of high-density storage optical disks and light sources for full-color displays. II-VI and nitride semiconductors are the most promising among these materials. Among II-VI semiconductors, ZnSe-based materials have a special importance [1], and quaternary $Zn_xMg_{1-x}S_ySe_{1-y}$ alloys are commonly used as cladding layers in II-VI blue-green laser diodes. This system—which was introduced a few years ago [2]—has the desirable property that its lattice parameter, a_0, and its fundamental band gap, E_g, can be tuned fairly independently by acting on the concentrations x and y. In spite of the technological importance of this material, extensive experimental studies of its electronic and optical properties over a wide range of compositions and of their dependence on the structural and thermodynamic equilibrium properties are still lacking.

We recently reported [3] on a theoretical study of the thermodynamical properties of this system, performed using state-of-the-art *ab-initio* methods. In that study the phase diagram of the quaternary alloy was determined, and the homogeneous alloy was found to be stable against segregation or the formation of ordered structures at temperatures typical of molecular-beam epitaxy (MBE) growth (≈ 550 K). Nevertheless, a large amount of short-range order (SRO) characterized by the occurrence of Zn-Se and Mg-S clustering among first-nearest neighbors was found to occur and to persist even at very high temperatures (≈ 1700 K).

In this Letter we report on the first extensive theoretical study of the electronic and optical properties of (Zn,Mg)(S,Se) alloys both in the case of the experimen-

tally well studied pseudo-binary ZnS_xSe_{1-x} system, and for the quaternary solid solution in conditions of lattice-matching to GaAs substrates. In the latter case the presence of the short range correlations will be shown to induce a small but significant opening of the fundamental band gap.

Our work is based on density-functional theory (DFT) within the local density approximation (LDA), and the plane-wave pseudopotential method. All the technical details of our calculations are the same as in Ref. [3]. DFT-LDA is known to underestimate electronic excitation energies, and many-body corrections should be considered, *e.g.* using the GW method [4]. In spite of this, the agreement between the *shape* of the band-structure predicted by the LDA and that measured experimentally is usually satisfactory, and semi-quantitative agreement can be simply obtained by a rigid upward shift of the conduction bands, using the so-called *scissor operator*.

Ideally, the study of the electronic properties of an alloy should proceed in three steps: *i)* the determination of the equilibrium structural properties of the system, including the relevant atomic correlations, as we obtained and discussed in Ref. [3]; *ii)* the calculation of the alloy band structure, taking into account the atomistic structure previously determined; *iii)* the inclusion of electronic correlations. It is still very hard to combine many-body calculations [4] with a proper description of disorder, and in the following we assume that disorder and quasi-particle effects can be treated independently: we deal explicitly with compositional disorder at the LDA level, and we add semi-empirically the many-body corrections by a simple interpolation of the scissor operators appropriate for the pure compounds.

Starting from the structural data determined in Ref. [3], we have calculated the electronic properties of the alloys using the *special quasi-random structures* approach [5]. The latter is based on the observation that—
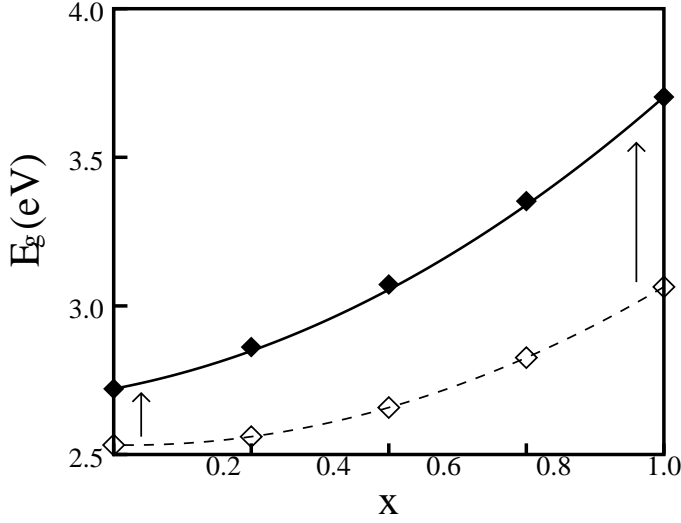
FIG. 1. Energy gap of the $\mathrm{Zn(S,Se)}$ pseudo-binary alloy as a function of sulphur concentration, x. Solid line: experimental data from Ref.[7]. Open diamonds: our theoretical results obtained neglecting many-body effects. Dashed line: quadratic interpolation to our theoretical results. Filled diamonds: theoretical results semi-empirically corrected for quasi-particle effects (see text).

for any given composition—atomic disorder mainly affects the electronic properties of an alloy through the short-range atomic structure. A disordered solid solution can thus be mimicked by using reasonably small supercells that reproduce the alloy SRO in the first few (typically, four or five) shells of neighbors. We have generalized the original method so as to account for any given short-range order [6], arbitrary compositions and double sub-lattice disorder. We have verified that atomic correlations beyond the fourth shell of neighbors affect only negligibly the band structure of the alloys presently studied. The supercell structures used in our simulations were thus obtained by a simulated-annealing procedure by which we searched among 64-atom simple-cubic structures the ones which give the most similar pair correlations up to the fourth shell of neighbors, as compared to those obtained from Monte Carlo simulations [3].

The electronic properties of the $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ pseudo-binary alloy, which are well characterized experimentally, have been studied by the above techniques, at three different concentrations, i.e. $x =0.25$, 0.50, 0.75. In Fig. 1 we display our results for the fundamental band gap of the alloy and compare them with available experimental data [7]. As previously discussed, LDA calculations systematically underestimate the optical gap. Adding a simple linear interpolation of the errors done at the pure-compound extremes, brings our theoretical predictions in very good agreement with experiments. Upon
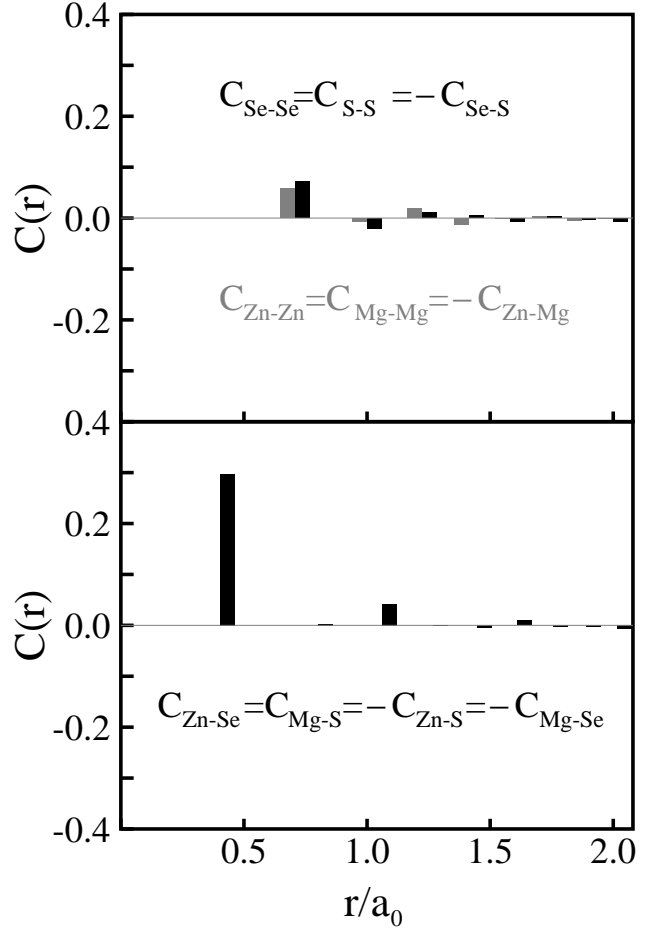

FIG. 2. Interatomic correlation functions in $\mathrm{Zn}_{\frac{1}{2}}\mathrm{Mg}_{\frac{1}{2}}\mathrm{S}_{\frac{1}{2}}\mathrm{Se}_{\frac{1}{2}}$ solid solutions (see Eq. (2)), as calculated in Ref. [3] for T= 550 K.

this semi-empirical correction, our data can be accurately described by the formula:

$$E_g(x) = E_g^{\mathrm{ZnSe}}(1-x) + E_g^{\mathrm{ZnS}}x + bx(1-x), \qquad (1)$$

where the curvature, commonly known as *bowing parameter*, is $b \approx 0.56$ eV. Our result is in good agreement with experiments [7,8], according to which 0.41 eV $\leq b \leq 0.68$ eV. It is worth noting that calculations done in the *virtual crystal approximation* (i.e. by neglecting disorder and averaging the atomic pseudopotentials in the anionic sub-lattice) would predict a small and *negative* bowing parameter: $b \approx -0.1$ eV. The accuracy by which our calculations predict the non-linear dependence of the band gap upon composition in the pseudo-binary $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ alloy indicates an almost linear dependence of quasi-particle effects on the concentration, which is encouraging for the study of the electronic properties of the quaternary alloy, where the available experimental data are scarcer.

The quaternary alloys displays a large amount of short-

TABLE I. Energy gap *vs.* compositions in (Zn,Mg)(S,Se). 'Virtual': theoretical results obtained within the virtual-crystal approximation. 'Random': super-cell calculations for the random alloy. 'SRO': supercell calculations done including SRO, but neglecting many-body effects. 'Corrected SRO': as above, but corrected for quasi-particle effects (see text). 'Expt': experimental data from Ref. [9].

x	y	Virtual	Random	SRO	Corrected SRO	Expt
0.50	0.50	2.96	2.57	2.64	3.52	3.56
0.75	0.13	2.68	2.48	2.50	3.00	3.00
0.84	0.00	2.55	2.43	2.44	2.78	2.82

range order. This is illustrated in Fig. 2 where we display the atomic correlation functions calculated in Ref. [3] at a temperature of 550 K and for $x = y = \frac{1}{2}$. The correlation function between two atomic species, X and Y, is defined as:

$$C_{\mathrm{XY}}(\mathbf{r}) = \langle \xi(\mathbf{r})\eta(0)\rangle - \langle \xi \rangle \langle \eta \rangle, \qquad (2)$$

where $\xi(\mathbf{r})$ and $\eta(\mathbf{r})$ are integer random variables whose value is 1 if the atomic site at position $\mathbf{r}$ is occupied by an atom of species X or Y respectively, and 0 otherwise; $\langle \cdot \rangle$ indicates the average over disorder; and $\langle \xi \rangle = x$ and $\langle \eta \rangle = y$ are the concentrations of the X and Y atomic species. The large positive value of the Zn–Se and Mg–S first-nearest neighbor correlations indicates a strong tendency to form ZnSe and MgS local clusters. This kind of clustering acts so as to reduce the elastic energy of the system because ZnSe and MgS have lattice parameters similar to each other and to that of the alloy ($a_{\mathrm{ZnSe}} = 10.57a.u.$ and $a_{\mathrm{MgS}} = 10.79a.u.$), but very different from those of ZnS and MgSe ($a_{\mathrm{ZnS}} = 10.09a.u.$ and $a_{\mathrm{MgSe}} = 11.32a.u.$). This tendency also shows in the second-nearest neighbor correlations which favor like cations and anions.

The electronic structure of the quaternary alloy has been studied for three different concentration pairs along the line of lattice-matching to GaAs (*i.e.* for pairs of concentrations, x and y, such that the average lattice parameter of the alloy is the same as that of GaAs).

In Table I we report the values of the fundamental gap as calculated taking into account SRO, neglecting SRO, and in the virtual-crystal approximation, and we compare these results with recent experimental data [9]. Quasi-particle effects are taken into account by the same kind of semi-empirical corrections described in the case of the pseudo-binary alloy. In the present quaternary case, the values of scissor operators for the four pure compounds are bi-linearly interpolated in-between. Our calculated values for the energy gaps are in very good agreement with experiments (within 0.04 eV). As it was the case for the Zn(S,Se) pseudo-binary alloy, the predictions of the virtual-crystal approximation are rather poor, resulting in too large a gap. The effect of SRO, as compared to the perfectly random solution, is to slightly open back the gap. The effect is small, but sizeable when disorder is maximum (*i.e.* for $x = y = \frac{1}{2}$). The effects of SRO on the alloy band structure can be understood qualitatively considering the actual alloy as a perturbation with respect to the appropriate virtual crystal (VC), as done by Baldereschi and Maschke [10] in an early study of the $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ alloy. Consider the actual alloy potential as a perturbation with respect to the VC potential:

$$V_{alloy}(\mathbf{r}) = V_{VC}(\mathbf{r}) + \Delta V(\mathbf{r}). \qquad (3)$$

To second order in the perturbation, the alloy band structure is given by

$$\epsilon_n(\mathbf{k}) = \epsilon_n^0(\mathbf{k}) + \sum_{n',\mathbf{k}'} \frac{|\langle n, \mathbf{k}|\Delta V|n', \mathbf{k}'\rangle|^2}{\epsilon_n^0(\mathbf{k}) - \epsilon_{n'}^0(\mathbf{k}')}, \qquad (4)$$

where $|n, \mathbf{k}\rangle$ are the virtual-crystal eigenvectors with energy $\epsilon_n^0(\mathbf{k})$, for the appropriate given composition pair (x, y). Since occupied (empty) states mostly interact with the other occupied (empty) states, that are closer in energy, the effect of the perturbation is to push the band edges in the gap region, thus reducing the virtual crystal gap, in agreement with our findings for $\mathrm{Zn_xMg_{1-x}S_ySe_{1-y}}$, random and correlated, quaternary alloy as well as for $\mathrm{ZnS_xSe_{1-x}}$ alloy. In the presence of SRO, this result can be generalized by showing that the magnitude of the gap reduction depends quadratically on the strength of the localized perturbations which transform the virtual crystal into the actual alloy, multiplied by the appropriate atomic correlation functions. From Fig. 2 it can be seen that the main difference between the correlated and the random alloy is that the former has a larger number of bond-length preserving Zn–Se and Mg–S nearest-neighbor pairs and a reduced number of bond-stretching Zn–S and Mg–Se nearest-neighbor pairs relative to the random alloy. The former type of perturbation of the virtual crystal is probably weaker than the latter, thus explaining the smaller closure of the VC gap in the correlated alloy as compared to the random case.

In order to better characterize the optical gap of the alloy, we consider the spectral weight:

$$A(E, \mathbf{k}) = \sum_n |\langle \psi_n|P(\mathbf{k})|\psi_n\rangle|^2 \delta(E - \epsilon_n), \qquad (5)$$

where ψ_n and ϵ_n are the wave-functions and energy levels of the supercell, and $P(\mathbf{k})$ is the projector over the states of quasi-momentum $\mathbf{k}$. We have found that the alloy wave-functions at the top of the valence and at the bottom of the conduction bands actually have a strong Γ character, thus indicating that the direct-gap nature of the pure materials is thus conserved also in the alloy. An analysis of the different atomic contributions to the DOS has been carried out by projecting the super-cell

eigenfunctions onto the atomic-like localized orbitals. We found that the states at the top of the valence band have a strong anionic character (26% centered on S and 67% on Se). The anionic character of the top of the valence band is a direct consequence of the ionic character of the alloy, while the larger contribution of the Se atomic orbitals is consistent with Harrison's tight binding tables [11] which indicate that the top of the valence band states of S-compounds lies about 0.5 eV below the analogous states of the corresponding Se-compounds. The low-lying conduction states are rather delocalized, with contributions from all the four atomic species and a slight prevalence of cationic character (28% Zn and 33% Mg).

a   Present address: *Center for Molecular Modeling, Dept. of Chemistry, University of Pennsylvania, Philadelphia, USA* Electronic address: saitta@cmm.chem.upenn.edu .

b   Electronic address : degironc@sissa.it .

c   Electronic address: baroni@sissa.it .

[1] *II-VI Blue/Green Light Emitters: Device Physics and Epitaxial Growth*, ed. by R. L. Gunshor and A. V. Nurmikko, Semiconductor and Semimetals **44**, Academic Press, (1997).

[2] H. Okuyama, *et al.*, Jpn. J. Appl. Phys. **30**, L1620 (1991); J. Cryst. Growth **117**, 139 (1992).

[3] A.M. Saitta, S. de Gironcoli, and S. Baroni, Phys. Rev. Lett. **80**, 4939 (1998).

[4] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985); R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986).

[5] A. Zunger, *et al.*, Phys. Rev. Lett. **65**, 353 (1990); S.-H. Wei, *et al.*, Phys. Rev. B **42**, 9622 (1990); K. C. Hass, L. C. Davis, and A. Zunger, Phys. Rev. B **42**, 3757 (1990).

[6] K. A. Mäder and A. Zunger, Phys. Rev. B **51**, 10462 (1995).

[7] A. Ebina, E. Fukunaga, and T. Takahashi, Phys. Rev. B **10**, 2495 (1974).

[8] L. G. Suslina, *et al.*, Fiz. Tekh. Poluprovodn. **11**, 1934 (1977)[Sov. Phys. Semicond. **11**, 1132 (1977)]; L. Soonckindt, *et al.*, Surf. Sci. **86**, 378 (1979); D. Etienne, M. de Murcia, and G. Bougnot, Thin Solid Film **70**, 285 (1980); R. Mach, *et al.*, Phys. Status Solidi B **109**, 607 (1982); A. A. El Shazly, *et al.*, Appl. Phys. A **36**, 51 (1985); H. Okuyama, Y. Kishita, and A. Ishibashi, Phys. Rev. B **57**, 2257 (1998).

[9] U. Lunz, *et al.*, Semicond. Sci. Technol. **12**, 970 (1997).

[10] A. Baldereschi and K. Maschke, Solid State Commun. **16**, 99, 1975.

[11] W. A. Harrison, *Electronic structure and the properties of solids*, Dover Publishing, New York, (1989).

[12] A.M. Saitta, PhD thesis, www.sissa.it/cm/thesis/1997/.